

Ab initio calculations of spectroscopic constants and properties of MgLi^+ and CaLi^+

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The ground states, with $^1\Sigma^+$ symmetry, of MgLi^+ and CaLi^+ molecular ions are investigated. The potential energy curve, spectroscopic constants and molecular property calculations are performed using correlation-consistent polarized valence triple zeta and quadrupole zeta basis sets. The non-relativistic and relativistic Hamiltonians together with the higher level of correlation methods are employed to examine the relativistic and correlation effects in the spectroscopic constants. The derived spectroscopic constants and dipole moments are compared with other calculations available in the literature. By maximizing the errors arising due to the choice of basis set and the correlation effects, we have quoted highly conservative error bars on the results.

Keywords: Potential energy curves, diatomic constants, dipole moment, quadrupole moment, dipole polarizability, MgLi^+ , CaLi^+ .

I. INTRODUCTION

Molecular spectroscopy, in particular the diatomic spectroscopy plays an important role for the understanding of physics and chemistry. In recent decades, study of cold and ultracold molecules is one of the most fertile field on the both theoretical and experimental aspects, due to its various applications in different areas such as optics, many-body physics, astrophysics, molecular physics, and quantum chemistry etc. For example, the controlled chemical reactions [1], quantum computing [2] and Bose-Einstein condensation (BEC) of molecules [3] can be achieved using optically trapped ultracold molecules, the vibrational-rotational transition frequencies can be measured precisely using state prepared molecules that are useful to study the variation in natural constants: proton-to-electron mass ratio $\mu \equiv m_p/m_e$ [4], the fine structure constant, α [5], and electric dipole moment (EDM) of an electron [6–8], etc. which further provides the important information for the grand-unification theories [9] and physics beyond the standard model, ultracold polar molecules can also be used to study the long-range dipole-dipole interactions [10].

A number of experimental techniques have been developed to generate neutral molecules: Buffer gas cooling [11] and electrostatic trapping [12] for the formation of cold molecules, photoassociation (PA) [13] and Feshbach resonance [14] for ultracold molecules, and many other methods have been discussed in Ref. [15] for high-precision measurements. The formation of cold molecular ions using radiative charge transfer (RCT), and radiative association (RA) process have been discussed in Ref. [16]. The (alkali-alkaline earth)⁺: RbCa^+ [17], and RbBa^+ [18] molecular ions are formed by direct association of the cold atom and a cold ion. The cold molecular ions can also be formed by sympathetic cooling using laser cooled atomic ions [19–21]. Recently, hybrid system of ultracold atom and ion, Li-Yb^+ has been studied

by Bissbort *et al.* [22] to imitate the solid-state physics. Kajita *et al.* [23] proposed the vibrational transition in N_2^+ to study the electron-proton mass ratio. Very recently, structural, electronic and dipolar properties of SrLi^+ have also been reported by Jellali *et al.* [24]. For the ionic species considered in current work, there is no experimental data available. Only theoretical works have been performed such as, for MgLi^+ : Pyykkö *et al.* [25] has reported the results for spectroscopic constants: bond length (R_e), dissociation energy (D_e), and harmonic frequency (ω_e), using Hartree-Fock (HF) and Møller-Plesset theory (MP2), Boldyrev *et al.* [26] has calculated R_e , ω_e at MP2 (full) level, and D_e at many-body perturbation theory of fourth-order (MP4), and quadratic configuration interaction with singles and doubles including perturbative triples (QCISD(T)) level, using 6-311+G* basis set for the ground state, *ab initio* study of ground and low lying excited states of MgLi and MgLi^+ have been reported by Y. Gao, and T. Gao [27] using full configuration interaction (FCI) and multi-reference configuration interaction (MRCI) method, the study of spectroscopic constants, potential energy curves (PEC's), permanent and transition electric dipole moment curves of ground and several excited states have been done by R. ElOualhazi and H. Berriche [28] using FCI method and for CaLi^+ : the perturbed-stationary-state method has been applied by Kimura *et al.* [29] to charge transfer in $\text{Li}^+ + \text{Ca}$ collisions for energies from 0.1 to 20 keV/amu and calculate the diatomic constants for the ground state, *ab initio* all-electron calculations for R_e , ω_e and ionisation energy of $X^1\Sigma^+$ ground state at QCISD(T) and complete active space self-consistent field-multi-reference all single- and double-excitation configuration interaction (CASSCF-MRCISD) level of correlation has been reported by Russon *et al.* [30], the study of electronic and vibrational properties of ground and excited states have been reported by Habli *et al.* [31] using FCI method.

In the present paper, we have performed the calculations of PEC's, the spectroscopic constants: R_e , D_e , ω_e , $\omega_e x_e$, B_e , and α_e , and the molecular properties: dipole moment (μ_e), quadrupole moment (Θ_{zz}), average po-

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larizability ($\bar{\alpha}$), polarizability anisotropy (γ) at equilibrium point, and z -component of polarizability at supermolecular limit, for the ground state of MgLi^+ and CaLi^+ ionic systems at different level of correlation with optimized basis sets. Objective of this work is to calculate the diatomic constants, and molecular properties accurately using high-level electronic structure methods. This work is the sequel of our previous study [32] where we had done the systematic calculations of the spectroscopic constants and molecular properties for the ground state of BeLi^+ molecular ion.

The present text is divided into four sections. After the introduction, section II briefly reports the different methods involved in the calculations. Section III includes the detailed description of the calculated results. Section IV summarizes the present work.

II. METHODOLOGY

CFOUR [33] and DIRAC15 [34] softwares are used throughout this paper. The systematic electronic structure calculations are carried out at self-consistent field (SCF), many-body perturbation theory (MP2), coupled cluster method with single and double excitations (CCSD) and CCSD with partial triples (CCSD(T)) level of correlation. The nuclear masses used for Li, Mg and Ca are 7.01600 a.u., 23.98504 a.u. and 39.96259 a.u., respectively. The uncontracted correlation consistent polarized valence (cc-pV) triple zeta (TZ) and quadrupole zeta (QZ) basis sets, [35–37], which are available in the DIRAC package are used together with the point nuclear distribution and C_{2v} point group symmetry. We have considered the z -axis as the internuclear axis of the molecules. All core, valence and also the virtual orbitals are kept active for the calculations of diatomic constants, and molecular properties reported in this paper. Further, The potential energy curves are plotted for the range of 2–30 Å distance with a step size of 1 Å and a small step size of 0.001 Å in the vicinity of equilibrium bond length. The dissociation energies are calculated as a difference between the energies at equilibrium point and those at a distance of 30 Å because the difference between the energies at 25 Å and 30 Å is less than 3 cm^{-1} for both MgLi^+ and CaLi^+ .

We have calculated the electronic ground state spectroscopic constants, and molecular properties at non-relativistic level using CFOUR code. The basis sets have been taken from the EMSL library [38]. The harmonic frequencies and anharmonic constants are calculated using second-order vibrational perturbation theory i.e., with VPT2 keyword in the CFOUR package. Evaluation of permanent dipole moment plays a key role in the study of interactions between ultracold molecules. Sign of the dipole moment depends on the assumption for the orientation of the interatomic axis. Negative values of the dipole moment confirms the excess of negative charge on the lighter atom, if we assume that the orientation of

the interatomic axis is along AA' , where A and A' represent the lighter and heavier atom, respectively. The dipole moment of the system is calculated via first-order derivative of energy with respect to the electric field as,

$$\mu = - \left(\frac{dE}{d\epsilon} \right)_{\epsilon=0} \quad (1)$$

The z -component of the quadrupole moment, Θ_{zz} is related to the other diagonal components by the relation,

$$\Theta_{zz} = -(\Theta_{xx} + \Theta_{yy}) \quad (2)$$

and for linear molecules, $\Theta_{xx} = \Theta_{yy}$. Therefore,

$$\Theta_{zz} = -2\Theta_{xx} \quad (3)$$

Using the parallel ($\alpha_{\parallel} = \alpha_{zz}$) and perpendicular components ($\alpha_{\perp} = \alpha_{xx}$ or α_{yy}) of dipole polarizability, we have obtained $\bar{\alpha}$ and γ as,

$$\bar{\alpha} = (\alpha_{\parallel} + 2\alpha_{\perp})/3 \quad (4)$$

and

$$\gamma = \alpha_{\parallel} - \alpha_{\perp}. \quad (5)$$

The relativistic calculations for ground state molecular constants are carried out using DIRAC15 package. After generating the reference state using SCF method, the energy calculations at MP2, CCSD and CCSD(T) are carried out using RELCCSD module. The Dirac-Coulomb Hamiltonian is used with the approximation proposed by Visscher [39] in which contribution from the (SS|SS) integrals are replaced by an interatomic (SS|SS) correction. The diatomic constants are calculated by second order differentiation of the potential energy curves. The harmonic frequencies, anharmonic constants and equilibrium rotational constants are obtained, respectively, using,

$$\omega_e = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}, \quad (6)$$

$$\omega_e x_e \cong \frac{\hbar \omega_e^2}{4D_e}, \quad (7)$$

and

$$B_e = \frac{h}{8\pi^2 c \mu R_e^2}, \quad (8)$$

where K , μ and c represent the force constant, the reduced mass of the constituent atoms of a molecule and the speed of light, respectively.

Errors in our calculations emerges from, the choice of basis set, and the higher-order terms of CC expansion neglected in the present work. The error due to the choice of basis set (Δ_1) can be approximated as the difference between the TZ and QZ values. Since the contribution from the higher order terms is not expected to be larger than the contribution from CCSD(T) level of correlation,

TABLE I. The computed spectroscopic constants for the electronic ground state of MgLi^+ and CaLi^+ molecular ions at different level of correlation using non-relativistic Hamiltonian and compared with the available results.

Molecule	Method/basis	R_e (a.u)	D_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	Reference
MgLi^+	SCF/TZ	5.599	6396.1	256.8	2.47	0.3537	0.0048	This work
	MP2/TZ	5.516	6595.9	264.5	2.46	0.3645	0.0049	This work
	CCSD/TZ	5.510	6634.6	265.8	2.49	0.3652	0.0047	This work
	CCSD(T)/TZ	5.509	6641.9	265.7	2.26	0.3655	0.0047	This work
	SCF/QZ	5.599	6409.3	256.6	2.49	0.3537	0.0049	This work
	MP2/QZ	5.501	6659.7	265.8	2.49	0.3665	0.0048	This work
	CCSD/QZ	5.497	6702.2	267.0	2.32	0.3670	0.0047	This work
	CCSD(T)/QZ	5.493	6712.4	267.3	2.30	0.3675	0.0046	This work
	Error bar	± 0.02	± 80.7	± 1.9	± 0.06	± 0.0025	± 0.0002	This work
	HF/6-31 G*	5.629	—	255	—	—	—	[25]
	MP2/6-31 G*	5.569	—	262	—	—	—	[25]
	MP2(full)/6-311 +G*	5.546	6470.5	261	—	—	—	[26]
	MRCI/AV5Z+Q	5.546	6508.9	263.5	2.37	0.3606	—	[27]
	MRCI/AV5Z+Q+DK	5.533	6557.3	266.4	2.48	0.3623	—	[27]
	MRCI/AVQZ+Q	5.548	6484.7	262.9	2.35	0.3603	—	[27]
	MRCI/AVQZ+Q+DK	5.544	6476.6	262.9	2.36	0.3608	—	[27]
	FCI/Gaussian	5.47	6575	264.22	2.63	0.372138	—	[28]
	SCF/STO-6G	5.633	—	—	—	—	—	[42]
CaLi^+	SCF/TZ	6.329	9734.4	240.2	1.79	0.2518	0.0024	This work
	MP2/TZ	6.178	9328.0	246.6	1.82	0.2643	0.0026	This work
	CCSD/TZ	6.189	9987.6	247.6	1.43	0.2633	0.0024	This work
	CCSD(T)/TZ	6.193	10008.5	245.8	1.60	0.2630	0.0024	This work
	SCF/QZ	6.327	9744.7	240.3	1.67	0.2520	0.0024	This work
	MP2/QZ	6.153	9428.0	246.2	1.68	0.2664	0.0025	This work
	CCSD/QZ	6.172	10083.3	246.8	1.37	0.2648	0.0023	This work
	CCSD(T)/QZ	6.170	10092.9	245.1	1.31	0.2650	0.0023	This work
	Error bar	± 0.025	± 94	± 2.4	± 0.23	± 0.0022	± 0.00012	This work
	FCI/STO's	6.20	8952.8	235	—	0.263	—	[29]
	QCISD(T)	6.274	10012.7	239	—	—	—	[30]
	CASSCF-MRCISD	6.272	—	239	—	—	—	[30]
	QCISD(T,full)	—	9678.7	—	—	—	—	[30]
	FCI/Gaussian	6.120	9973.27	242	—	—	—	[31]

we have taken the entire contribution from the perturbative triples as an error (Δ_2) due to higher order correlation effects. Therefore, the final value of the calculated property is,

$$f_{final} = f_{CCSD(T)} \pm |\Delta_1| \pm |\Delta_2| \quad (9)$$

where $f_{CCSD(T)}$ is the property of interest at CCSD(T) level using QZ basis set.

III. RESULTS AND DISCUSSION

Atomic units for distance ($1 \text{ a.u.} = 0.52917721 \text{ \AA}$) and dipole moment ($1 \text{ a.u.} = 2.54174691 \text{ D}$) will be used throughout the paper.

Figures 1 - 2 show the PEC's of MgLi^+ and CaLi^+ molecular ions using non-relativistic and relativistic Hamiltonian, respectively, with QZ basis set. The computed results at non-relativistic level in the present work and

available results in the literature are tabulated in Table I. The calculated values of the spectroscopic constants using the relativistic Hamiltonian are given in Table II. The results for the molecular properties, in the non-relativistic case are shown in Table III. Also, the parallel-component of the dipole polarizability at super-molecular limit, i.e. at a bond distance of 100 a.u. , denoted as α_{100} , is reported in the last column of Table III. Polarizabilities in the super-molecular limit are compared with $\alpha_A = \alpha_X + \alpha_{Li^+}$ ($X = \text{Mg, Ca}$), i.e. the sum of the atomic polarizabilities. These values of atomic polarizabilities have been taken from Ref. [40, 41]. The calculated values of the dipole moment at equilibrium point are negative for both MgLi^+ , and CaLi^+ molecular ions. However, we have reported the absolute values at equilibrium internuclear distances in Table III. Our results for dipole moment at equilibrium point are compared with those extracted from the dipole moment curves available in the literature. Quadrupole moments and electric dipole polarizabilities are reported here for the first time to the best of our knowledge.

TABLE II. The computed spectroscopic constants for the electronic ground state of MgLi^+ and CaLi^+ molecular systems at different level of correlation using QZ basis set, in the relativistic case.

Molecule	Method/basis	R_e (a.u.)	D_e (cm^{-1})	ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	B_e (cm^{-1})
MgLi^+	SCF/TZ	5.597	6377.7	288.5	3.26	0.3542
	MP2/TZ	5.512	6579.5	288.5	3.16	0.3653
	CCSD/TZ	5.507	6618.3	303.5	3.48	0.3659
	CCSD(T)/TZ	5.505	6625.7	276.7	2.89	0.3662
	SCF/QZ	5.595	6390.8	233.2	2.13	0.3545
	MP2/QZ	5.497	6644.5	288.5	3.13	0.3673
	CCSD/QZ	5.493	6685.6	303.5	3.44	0.3678
	CCSD(T)/QZ	5.49	6695.9	288.5	3.11	0.3682
	Error bar	0.018	80.5	26.8	0.55	0.0024
CaLi^+	SCF/TZ	6.321	9648.2	262.9	1.79	0.2526
	MP2/TZ	6.168	9323.6	266.7	1.91	0.2653
	CCSD/TZ	6.181	9911.0	218.9	1.21	0.2642
	CCSD(T)/TZ	6.185	9933.47	251.1	1.59	0.2638
	SCF/QZ	6.321	9660.3	262.9	1.79	0.2526
	MP2/QZ	6.147	9355.0	261.0	1.82	0.2671
	CCSD/QZ	6.166	9999.4	247.8	1.53	0.2655
	CCSD(T)/QZ	6.164	10009.8	256.4	1.64	0.2656
	Error bar	0.023	86.73	13.9	0.16	0.0019

TABLE III. Dipole moments, quadrupole moments and static dipole polarizabilities of MgLi^+ and CaLi^+ .

Molecule	Method/basis	$ \mu_e $ (a.u.)	θ (a.u.)	α_{\parallel} (a.u.)	α_{\perp} (a.u.)	$\bar{\alpha}$ (a.u.)	γ (a.u.)	α_{100} (a.u.)
MgLi^+	SCF/TZ	2.086	20.045	84.464	61.236	68.979	23.228	81.386
	MP2/TZ	2.112	19.308	79.383	57.217	64.606	22.165	73.387
	CCSD/TZ	2.139	19.165	78.408	57.216	64.280	21.192	72.273
	CCSD(T)/TZ	2.146	19.122	78.145	56.975	64.032	21.170	71.823
	SCF/QZ	2.085	20.041	84.485	61.339	69.054	23.146	81.544
	MP2/QZ	2.103	19.214	78.642	57.128	64.299	21.514	73.652
	CCSD/QZ	2.129	19.075	77.885	57.151	64.062	20.734	72.938
	CCSD(T)/QZ	2.135	19.017	77.533	56.863	63.753	20.669	72.462
	Error bar	0.017	0.163	—	—	0.588	0.566	1.115
CaLi^+	MRCI/AV5Z+Q+3DK [27]	2.126	—	—	—	—	—	—
	CI/Gaussian [28]	3.075	—	—	—	—	—	—
	SCF/TZ	1.441	24.140	181.719	117.212	138.714	64.507	185.046
	MP2/TZ	1.827	23.401	165.102	102.065	123.077	63.037	144.279
	CCSD/TZ	1.695	23.344	163.684	108.221	126.708	55.463	163.853
	CCSD(T)/TZ	1.751	23.328	161.008	107.309	125.209	53.700	161.862
	SCF/QZ	1.439	24.121	181.668	117.329	138.776	64.339	185.461
	MP2/QZ	1.814	23.182	162.911	101.711	122.111	61.199	143.741
	CCSD/QZ	1.685	23.157	162.699	107.947	126.198	54.752	163.386
	CCSD(T)/QZ	1.748	23.120	159.409	106.738	124.295	52.671	160.812
	Error bar	0.066	0.245	—	—	2.817	3.11	3.624
	FCI/Gaussian [31]	2.713	—	—	—	—	—	—

A. MgLi^+

At SCF level, our findings for diatomic constants using QZ basis set are significantly close to those reported in Ref. [25, 42] (less than 1% error). The calculated MP2 results using QZ basis set in the current work compares well with those calculated in Ref. [25] at the

same level of correlation. The difference between our recommended results, highlighted in bold fonts and the MRCI results quoted in Ref. [27], at same level of basis set is not more than 4% in all spectroscopic constants. Our final values of the spectroscopic constants, at non-relativistic level, are in good agreement with those reported in Ref. [28]. The difference in our relativistic and non-relativistic calculations is about, 0.003 *a.u* for

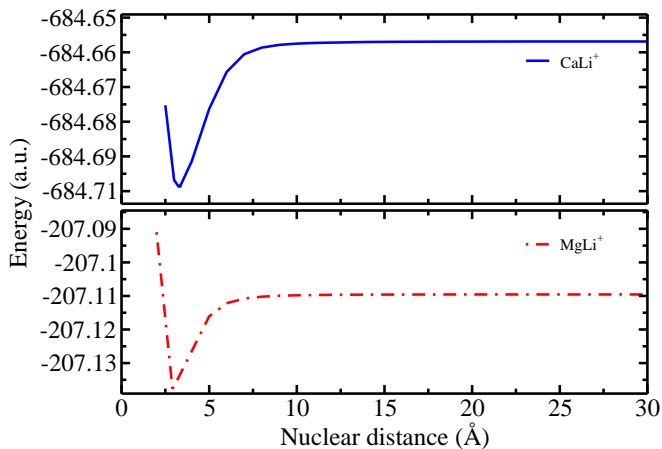


FIG. 1. (colour online) Potential energy curves for the ground state of MgLi^+ and CaLi^+ molecular ions at CCSD(T) level of correlation using QZ basis set, in the non-relativistic case.

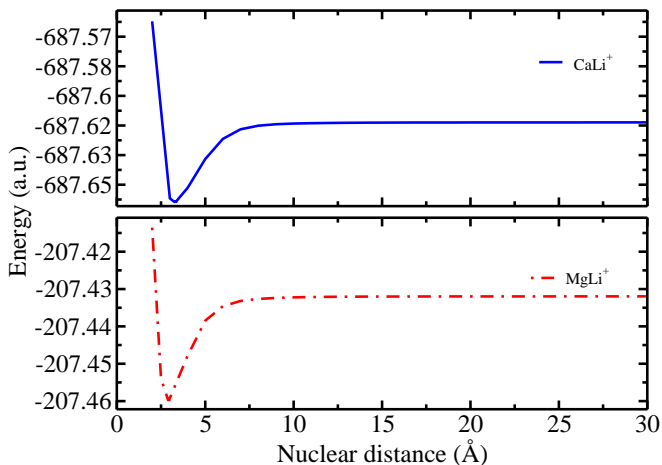


FIG. 2. (colour online) Potential energy curves for the ground state of MgLi^+ and CaLi^+ molecular ions at CCSD(T) level of correlation using QZ basis set, in the relativistic case.

R_e , 16.5 $a.u.$ for D_e , 21.2 cm^{-1} for ω_e , 0.81 cm^{-1} for $\omega_e x_e$, and 0.0007 cm^{-1} for B_e , at CCSD(T) level of correlation using QZ basis set. In Ref. [27] the dipole moment of MgLi^+ is $\sim 2.126 a.u.$ at equilibrium point, which is close to our value of 2.135 $a.u.$ The calculated value of dipole moment in Ref. [28] is $\sim 3.075 a.u.$ at equilibrium internuclear distance is larger than our result. The value of polarizability at super molecular limit in the present calculation, $= (72.462 \pm 1.115) a.u.$ compares well with the sum of atomic polarizabilities, $\alpha_A = \alpha_{Mg} + \alpha_{Li^+} = 73.41 + 0.191 = 73.601 a.u.$, at

the same level of theory.

B. CaLi^+

According to the spectroscopic study of Russon *et al.* [30] at CASSCF-MRCISD level, the CaLi^+ molecular ion has equilibrium bond length $R_e = 6.272 a.u.$, and harmonic frequency $\omega_e = 239 cm^{-1}$, which are close to our values of 6.172 $a.u.$, and 246.8 cm^{-1} respectively, at CCSD level using QZ basis set. The non-relativistic results, given in bold fonts are agreed extremely well with those reported in Ref. [30, 31] at QCISD and FCI level of correlation (less than 3%). Using CCSD(T) level of theory and QZ basis set, relativistic and non-relativistic results are differ by, 0.006 $a.u.$ for R_e , 83.1 cm^{-1} for D_e , 11.3 cm^{-1} for ω_e , 0.33 cm^{-1} for $\omega_e x_e$, $\sim 10^{-4} cm^{-1}$ for B_e . Habli *et al.* reported the only available *ab initio* study on the dipole moment for CaLi^+ ionic species. In this work the value of the dipole moment at equilibrium bond length is $\sim 2.713 a.u.$, which is $\sim 0.97 a.u.$ larger than our results of 1.748 $a.u.$ The sum of individual atomic polarizabilities, $\alpha_A = \alpha_{Mg} + \alpha_{Li^+} = 158.6 + 0.191 = 158.791 a.u.$ is somewhat smaller than our result of polarizability at super-molecular limit $= (160.812 \pm 3.624) a.u.$

IV. SUMMARY

In conclusion, we have done the *ab initio* study of spectroscopic constants and molecular properties for electronic ground state of MgLi^+ and CaLi^+ , using non-relativistic and relativistic Hamiltonian. The reported results for diatomic constants and dipole moments compared well with the existing results in the literature. Additionally, quadrupole moments and components of dipole polarizabilities for the considered molecular ions are reported here for the first time. Maximum possible error bars are also reported on the spectroscopic constants and molecular properties.

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